21 #
2/17/69
LA-3995

661

MASTER

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

The Solubilities of Selected Elements
in Liquid Plutonium
XIII. Titanium and Manganese

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

This report expresses the opinions of the author or authors and does not necessarily reflect the opinions or views of the Los Alamos Scientific Laboratory.

Printed in the United States of America. Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

Report written: August 23, 1968

Report distributed: January 27, 1969

The Solubilities of Selected Elements
in Liquid Plutonium
XIII. Titanium and Manganese

by

David F. Bowersox

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

THE SOLUBILITIES OF SELECTED ELEMENTS IN
LIQUID PLUTONIUM. XIII. TITANIUM AND MANGANESE

by

David F. Bowersox

ABSTRACT

The solubility of titanium in liquid plutonium increases with temperature from 1.1 wt % Ti at 700°C to 10.6 wt % Ti at 1000°C. At 700 and 750°C, the data fit the equation

$$\log N_{\text{Ti}} = 1.90 - 5.03 \times 10^3 T^{-1},$$

where N_{Ti} is the mole fraction of Ti in solution at the absolute temperature T . Above the peritectic temperature of 770°C, the data fit the equation

$$\log N_{\text{Ti}} = 0.74 - 1.49 \times 10^3 T^{-1}.$$

The solubility of manganese in liquid plutonium increases from 9.3 wt % Mn at 850°C to 21.0 wt % Mn at 1000°C. The data fit the equation

$$\log N_{\text{Mn}} = 1.52 - 2.27 \times 10^3 T^{-1},$$

where N_{Mn} is the mole fraction of Mn in solution.

INTRODUCTION

The studies of the solubilities of titanium and manganese in liquid plutonium continue a program designed to measure the solubilities of selected elements in plutonium and plutonium alloys. The solubilities of C, Ta, W, Re, Nb, Mo, V, Tm, Zr, and Cr in liquid plutonium have been reported.⁽¹⁻⁷⁾ The solubilities of these elements increased with temperature, and empirical equations were constructed from the solubility data by least-squares calculations. These were of the form

$$\log N_i = A - B \times 10^3 T^{-1}, \quad (1)$$

where N_i is the mole fraction of element i in solution, A and B are empirical constants, and T is the absolute temperature. These solutes were usually of limited solubility; in all cases the solubility was less than 10 at.%. Both the Ti-Pu and Mn-Pu phase diagrams indicate higher solubilities and more complex binary systems than those observed in most of the earlier studies.^(8,9) A peritectic melting point occurs in the Ti-Pu binary at 770°C and 22 at.% Ti. From the liquidus line, the Ti solubility apparently increases from 5 at.% at 700°C to 37 at.% at 1000°C.⁽⁸⁾ A

Table I

Analyses of Pu, Ti, and Mn

Element	ppm in Pu ^a	ppm in Ti	ppm in Mn	Element	ppm ^a in Pu	ppm in Ti	ppm in Mn
Li	< 0.005	< 1	< 10	Co	< 1	< 10	< 100
Be	< 0.001	< 3	< 10	Zn	< 10	< 300	< 10
Na	1	< 10	< 10	Am	72	...	...
Mg	2	< 10	< 100	O	10	190	1700
Ca	< 2	< 10	< 100	Mo	< 1	< 30	< 10
Al	1	< 10	< 10	W	48 ± 1	...	...
La	< 1	..	...	Th	< 15	...	...
Si	6	< 30	30	Ta	< 25	...	...
Pb	< 1	< 10	< 30	Zr	< 10	< 100	< 10
Cu	2	10	< 10	H	10 ± 5	...	...
Ni	1	30	< 10	C	10 ± 10	...	...
Cr	< 1	100	< 10	F	< 2	...	...
B	< 0.5	< 10	< 10	V	< 30	30	...
Mn	< 0.5	10	99.8%	Fe	20	100	< 10
Sn	< 1	< 10	< 10	Pu	100.00%	...	...

^aParts per million parts Pu, by wt.

eutectic melting point occurs in the Mn-Pu binary system at 520°C and 10 at. % Mn. The compound PuMn₂ has been reported. From the liquidus line, the Mn solubility is estimated as increasing from 21 at. % at 700°C to 46 at. % Mn at 1000°C.⁽⁹⁾

EXPERIMENTAL

Electrorefined Pu,⁽¹⁰⁾ crystal bar Ti, and high purity Mn were used for this study. The analyses of these elements are summarized in Table I. The equipment and the procedures employed have been described in earlier reports.⁽¹⁾ The samples, which contained Pu and either Ti or Mn, were dissolved, and aliquots were analyzed for the solute element. The estimated relative standard deviation of each analytical method is 2 % in the concentration ranges measured.^(11,12)

Results

Samples were withdrawn from Pu-Ti and Pu-Mn mixtures at timed intervals to establish the rates of approach to saturation. Results at 850°C, which are typical of those throughout this temperature range, are shown in Table II. The Pu-Mn system reached satura-

Table II

Solubilities of Ti and Mn in Liquid Pu at 850°C
(Approach from undersaturation)

Time, hr	Solubility, wt %	
	Ti	Mn
4.0	2.9	8.4
7.0	3.1	8.8
24.0	3.8	9.4
30.0	4.1	9.2
48.0	6.4	9.4
72.0	6.4	9.2
96.0	6.6	...

tion within 24 hr; the Pu-Ti system, within 48 hr. The reversibility of these systems was demonstrated by approaching saturation from both above and below. The data were independent of the direction of approach.

The solubility of Ti in liquid Pu was then measured as a function of temperature from 700 to 1000°C under reversible conditions. The results are summarized in Table III. Dilatometric, metallographic, and thermal arrest observations agree with these results below

Table III
The Solubilities of Ti and Mn in Liquid Pu

Temperature, °C	Average Solubility			
	Wt % Ti	At. % Ti	Wt % Mn	At. % Mn
700	1.14	5.4	....	....
750	2.11	9.7	....	....
800	5.5	22.5	....	....
850	6.6	26.0	9.3	30.9
900	7.5	29.1	....	....
950	9.2	33.6	16.0	45.7
1000	10.6	37.2	21.0	53.6

770°C.⁽¹³⁾ The estimates of solubility from the liquidus line of the phase diagram⁽⁸⁾ are also in agreement with these data.

Measurements of the Mn solubility were limited to three temperatures, 850, 950, and 1000°C. The results, summarized in Table III, show clearly the high solubility of Mn, as would also be predicted from the phase diagram.⁽⁹⁾

Discussion

The solubility of Ti in liquid Pu can be represented by two temperature-dependent equations. From 700 to 770°C,

and from 770 to 1000°C

In Fig. 1, the logarithm of the atom percent Ti in solution is plotted against the inverse of the absolute temperature. The peritectic point (at 770°C) is reflected by a change in the slope. Least-squares calculations on the data were divided into two groups, those below and those above the peritectic temperature. Below 770°C, the data fit the equation

$$\log N_{\text{Ti}} = 1.90 - 5.03 \times 10^3 T^{-1}, \quad (4)$$

where N_{Ti} is the mole fraction of Ti in a saturated solution at absolute temperature T . Above 770°C, the data fit the equation

$$\log N_{\text{Ti}} = 0.74 - 1.49 \times 10^3 T^{-1}. \quad (5)$$

If the first constants in Eq. (4) and (5) represent entropy and the second, enthalpy, both must have been

Fig. 1. Atom percent solubility of Ti and Mn vs. reciprocal temperature.

altered during the peritectic transition at 770°C.

The equilibrium solubility reaction in the Pu-Mn system in the concentration and temperature range of interest should be

The average Mn solubilities are plotted as the logarithms of the atom percent Mn against the inverse of the absolute temperature in Fig. 1. The resulting line, by least-squares calculations, fits the equation

$$\log N_{\text{Mn}} = 1.52 - 2.27 \times 10^3 T^{-1}. \quad (7)$$

The high solubilities and the limited number of temperatures at which measurements were made limit the usefulness of Eq. (7) in estimating other points in the Pu-Mn system.

ACKNOWLEDGMENTS

The author thanks J.A. Leary for his advice and encouragement, and Lorraine E. Thorn, W.J. Baughman, and J.W. Dahlby for performing chemical analyses for this study.

REFERENCES

1. D. F. Bowersox and J. A. Leary, J. Nucl. Mater., 21, 219 (1967).
2. D. F. Bowersox and J. A. Leary, "The Solubilities of Selected Elements in Liquid Plutonium. VII. Niobium," LA-3436 (1965).
3. D. F. Bowersox and J. A. Leary, "VIII. Molybdenum," LA-3523 (1966).
4. D. F. Bowersox and J. A. Leary, "IX. Vanadium," LA-3594 (1966).
5. D. F. Bowersox and J. A. Leary, "X. Thulium," LA-3623 (1966).
6. D. F. Bowersox and J. A. Leary, "XI. Zirconium," LA-3742 (1967).
7. D. F. Bowersox, "XII. Chromium," LA-3850 (1968).
8. D. M. Poole, M. G. Bale, P. G. Mardon, J. A. C. Marples, and J. L. Nichols, in Plutonium 1960, E. Grison et al., Eds., Cleaver-Hume Press, London, 1960, p. 277-8.
9. F. W. Schonfeld, in The Metal Plutonium, A. S. Coffinberry and W. N. Miner, Eds., Univ. of Chicago Press, Chicago, 1961, p. 240.
10. L. J. Mullins and J. A. Leary, Ind. Eng. Chem. Process Design Develop., 4, 394 (1965).
11. K. S. Bergstresser, Anal. Chem., 29, 532 (1957).
12. G. R. Waterbury, private communication.
13. C. C. Land, private communication.